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#### **Simultaneous SAXS/FT-IR Studies of Reaction Kinetics and Structure Development During Polymer Processing**

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In a novel combination, synchrotron radiation small angle X-ray scattering (SAXS) and Fourier Transform infra-red spectroscopy (FT-IR) experiments have been performed on a series of model segmented polyurethanes [1]. This combination of techniques is potentially a very powerful research tool, not only for polymer research, but for a wide variety of research fields including biological gel formation, food processing and conformational changes in proteins.

The major theme of the research group's work is studying the *in-situ* development of structure during the processing of multiphase polymers, in particular polyurethanes [1-6]. These materials are of great

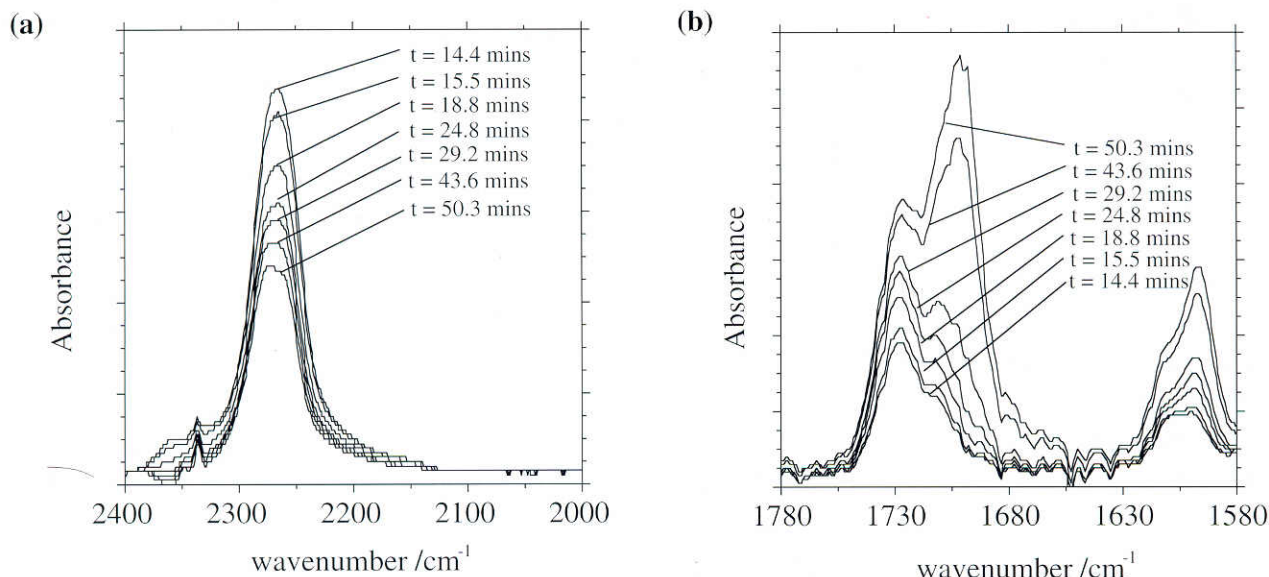
commercial utility combining unique mechanical properties with ease of processing. Polyurethanes are formed by the reaction between a diisocyanate, a short chain diol and a macrodiol. The development of polymer morphology is complex [1,4] and the process can be best described as a reaction-induced phase separation. The morphology formed is determined by the kinetic competition between polymerization and microphase separation [5]

The experimental configuration, methods and chemical systems studied are described in detail elsewhere [1]. FT-IR spectroscopy is used to monitor the reaction chemistry and SAXS is used to monitor the development of polymer morphology on the sizescale of 20-1000 Å. Figure 1 shows the decay in the isocyanate absorbance (which correlates with the polymerization kinetics) and the growth in the carbonyl absorbances [1,6]. Figure 2 shows the SAXS data, which indicate the development of polymer structure with a length scale of  $\approx 118$  Å. Figure 3 shows the onset of microphase separation detected by both SAXS and FT-IR. Microphase separation precedes hydrogen bonding and is driven by the free energy of mixing. This causes the groups that are capable of hydrogen bonding to achieve a locally high concentration and their rate of association increases. The hydrogen bonding is thus parasitic and *not* the driving force.

#### **References**

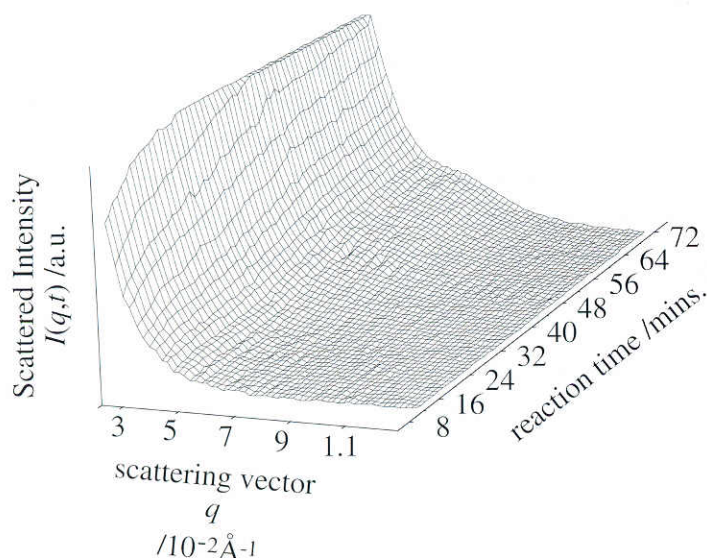
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**Figure 1.**

(a) Absorbance versus frequency illustrating the decay in the intensity of the isocyanate absorbance ( $\approx 2270 \text{ cm}^{-1}$ ) at selected times for a model segmented block copolyurethane at  $35 \pm 1^\circ \text{C}$ . (b) Absorbance versus frequency illustrating the carbonyl region of the mid-infrared spectrum, at selected time frames for the same model segmented block copolyurethane at  $35 \pm 1^\circ \text{C}$ .



**Figure 3.**

The SAXS relative invariant,  $Q' = \int I(q,t) q^2 dq$  and the normalised FT-IR absorbance associated with hydrogen-bonded urethane are plotted against time, for a model segmented block copolyurethane investigated at  $25 \pm 1^\circ \text{C}$ . Tangents have been fitted to both data sets in order to estimate the onset times for microphase separation ( $t_\phi$ ) and hydrogen bonding ( $t_H$ ). The values of  $t_\phi$  and  $t_H$  are  $43 \pm 1$  and  $47 \pm 1$  minutes respectively. The perfect time correlation between the two techniques confirms unambiguously that microphase separation precedes hydrogen bonding in the reactive processing of this polyurethane block copolymer.

**Figure 2.**

The time evolution of the SAXS pattern is illustrated as a time-stack of the scattered intensity,  $I(q,t)$ , versus scattering vector,  $q$ . The data were recorded in frames of 60 s. For clarity, only every fourth frame of data is shown. Initially there is little scattering and the peak that starts to grow at  $q = 0.053 \text{ \AA}^{-1}$  after  $\approx 40$  minutes is evidence for the structural development in the material with a linear dimension of  $\approx 118 \text{ \AA}$ .

